ULTRASONIC ABSORPTION IN LIQUID OXYGEN

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by

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Abstract of

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An experimental apparatus was constructed in order to measure ultrasonic absorption as a function of temperature in cryogenic fluids in the liquid nitrogen temperature range with particular interest in measuring the effect of a magnetic field on the sound absorption in liquid oxygen. Measurements were made at 50 MHz in liquid oxygen over the temperature range 65° - 85°K and in liquid nitrogen at 70° and 75°K. The values of the absorption coefficients (α/ν^2) obtained for liquid oxygen ranged from 10.3 to 12.2×10^{-17} sec^2cm^{-1} ± 10% and for liquid nitrogen, 13.2 to 14.3×10^{-17} sec^2cm^{-1} ± 10%. These are approximately 20% higher than those obtained previously (J. K. Galt, Journal of Chem. Phys. 16, 505 (1948)) and about 60% higher than those calculated from classical theory. The temperature dependence predicted by theory is observed in liquid oxygen. When liquid oxygen was subjected to magnetic field of 10 kG, the values of α/ν^2 obtained were within 4% of the zero-field values. The excess absorption observed in the zero-field case is attributed to a systematic error in the apparatus and to the possibility of the presence of relaxation phenomena.

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is accepted in its present form by the Department of Physics as satisfying the thesis requirement for the degree of Master of Science.

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I. INTRODUCTION

The measurement of sound absorption in the liquefied gases (N_2, O_2, Ar, He, H_2) has been an area of relatively little investigation. This is probably because of the fact that the values of the few measurements that have been made agree so closely to the classical theoretical values of sound absorption, that it has been felt that little new information would be ascertained by extensive research in this area. An exception to this is liquid helium in which relaxation phenomena have been observed at very low temperatures (0.085°K) and at the λ point.[1]

Of all the gases listed above, only oxygen has the peculiarity of being paramagnetic. This being the case, a magnetic field imposed on oxygen changes its viscosity and boiling points by about 1%.[2,3] In 1938, Van Itterbeek reported that the sound absorption in gaseous oxygen was reduced by 20% when placed in a magnetic field of 5000 gauss.[4] Up to now, the only sound absorption measurements made in liquid oxygen were performed by Galt[5]; whose values were within experimental error of the classical absorption values. However, he found that at the three temperatures at which he made his observations the absorption coefficients were identical. Also, when he placed liquid oxygen in a magnetic field of 1000 gauss, no effect on the sound absorption was observed.

The peculiar lack of temperature dependence of Galt's measurements together with the limited number of values obtained suggested that these measurements should be repeated over a more complete temperature spectrum. The purpose of this project, then, was to construct an apparatus for the measurement of sound absorption in liquefied gases in the temperature range of liquefied oxygen and in particular measure the effects of a magnetic field on the sound absorption in liquid oxygen.

II. THEORETICAL

The theoretical value of the sound absorption coefficient is obtained by considering the effect of viscosity, heat conduction, and relaxation processes on a sound wave passing through a fluid. The first two lead to the "classical" sound absorption coefficient while the latter accounts for the major part of sound absorption in many substances; however, in the case of the liquefied gases, the classical value seems to dominate.

To derive the classical sound absorption coefficient, it is necessary to apply the fundamental equations of fluid mechanics and thermodynamics to a viscous, heat conducting fluid element. First of all, the continuity equation demands that the flux of fluid through a volume element must be equal to the time rate of change of the fluid density. The most general form of the continuity equation is:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = m\rho \tag{1}$$

Where ρ is the density (gm/cm^3),

$\vec{V}$ is the velocity with components u, v, w,

and m is the strength of any sources or sinks within the fluid element under consideration.

For one dimensional flow with no sources or sinks, Eq. (1) will reduce to:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x}(\rho u) \tag{2}$$

Instead of using the density as a variable, the related variable called condensation is usually used and is defined by:

$$S \equiv \frac{\rho - \rho_o}{\rho_o} \tag{3}$$

where ρ is the density of the fluid at the time it is perturbed by the sound wave and ρ_o is the equilibrium density. With this definition Eq. (2) becomes:

$$\frac{\partial S}{\partial t} = -\frac{\partial u}{\partial x} \tag{4}$$

Second, the momentum equation can be derived by applying Newton's second law to a fluid element, i.e.;

$$\vec{F} = \int \rho \frac{D\vec{V}}{Dt} d\tau \tag{5}$$

where D/Dt denotes the total or substantive time derivative. For any fluid element the forces on that element can be divided into body forces, such as gravitational or electromagnetic forces, and surface forces such as pressure and viscous frictional forces per unit area. Normally the pressure and the frictional forces per unit area are components of the stress tensor of a fluid element, $\overleftrightarrow{\sigma}$. The stress tensor used in fluid flow is analogous to the corresponding tensor used in the theory of elasticity; however, the important difference is that for solid bodies, Hooke's Law relates the stress to the strain of the body whereas in fluid motion, the stress is related to the rate of strain of the fluid element. This relationship is derived in any standard fluid mechanics text[6]; in the most general form of the tensor a component of the stress is given by

$$\sigma_{ij} = (-p + \frac{\lambda}{2} e_{kk})\delta_{ij} + \eta e_{ij} \tag{6}$$

where the e_{ij} are the components of the rate of strain tensor which are defined as:

$$e_{ij} \equiv \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \text{ which implies } e_{kk} = 2\nabla \cdot \vec{V} \quad . \tag{7}$$

Also, λ and η are the first and second viscosity coefficients, respectively and P is related to the thermodynamic pressure as will be shown below.

For an ideal, inviscid fluid, the only stresses present are the pressure forces normal to the sides of the fluid element. The trace of the matrix elements defined in Eq. (6) would be in this case:

$$\sigma_{kk} = -3P \quad . \tag{8}$$

Therefore, the thermodynamic pressure is $P = -\sigma_{kk}/3$. It is convenient to maintain the same definition of pressure in the viscous case. For a viscous fluid the trace of Eq. (6) yields:

$$\sigma_{kk} = 3(-P + \frac{\lambda}{2} e_{kk}) + \eta e_{kk} \tag{9}$$

Consequently, the pressure is,

$$p = -\frac{\sigma_{kk}}{3} = -P + \left(\frac{\lambda}{2} + \frac{\eta}{3}\right) e_{kk} \tag{10}$$

In order to follow the classical derivation, the Stoke's assumption is usually applied to Eq. (10) at this point. In essence, this states that the only frictional forces present in a fluid element are those caused by the shearing motion of the fluid and none are present as a result of pure volume dilatation. In order for this to be true, the bulk viscosity coefficient $\left(\frac{\lambda}{2} + \frac{\eta}{3}\right)$ must be zero. With this condition, Eq. (6) becomes

$$\sigma_{ij} = -(p + \eta \frac{e_{kk}}{3}) \delta_{ij} + \eta e_{ij} \tag{11}$$

where η is called the shear viscosity coefficient.

Now Eq. (5) can be written as

$$F = \int \rho \frac{D\vec{V}}{Dt} d\tau = \int \rho \vec{f} \, d\tau + \int \vec{T} dA$$

where the first term on the right is due to the body forces with $\vec{f}$ equal to the body force per unit volume and the second term is due to the surface forces where

$$T_i \equiv \sigma_{ij} n_j \tag{12}$$

and n_j is the unit normal in the jth direction. By applying Stokes' theorem to the latter term, the surface integral is transformed into a volume integral and since the volume is arbitrary, the equation of motion in differential form is

$$\rho \frac{D\vec{V}}{Dt} = \rho\vec{f} - \vec{\nabla}\rho + \frac{\eta}{3} \nabla(\nabla\cdot\vec{V}) + \eta\nabla^2 \vec{V} \tag{13}$$

For the one dimensional case, neglecting body forces, this becomes

$$\rho \frac{\partial}{\partial t}(u) = -\frac{\partial p}{\partial x} + \frac{4}{3}\eta \frac{\partial^2 u}{\partial x^2} \tag{14}$$

The energy relationships involved in fluid motion are found through use of the first law of thermodynamics

$$dQ = dU + dW = c_v dT - \frac{p_o}{\rho_o{}^2} d\rho \tag{15}$$

To a first approximation, the thermodynamic processes involved in small amplitude acoustics are assumed to be adiabatic; however, when dealing with absorption, the amount of heat conducted through the fluid via diffusion must be considered. The heat dissipation due to the shearing stresses is a second order effect and can be safely neglected. The rate of heat conduction is given by the diffusion equation

$$\frac{dQ}{dt} = \frac{\kappa}{\rho_o} \frac{\partial^2 T}{\partial x^2} \tag{16}$$

where κ is the thermal conductivity coefficient (cal/cm.sec.°K).

T is the absolute temperature (°K).

Now Eq. (15) can be modified to give the rate of heat conduction

$$\frac{\kappa}{\rho_o}\frac{\partial^2 T}{\partial x^2} = c_v \frac{dT}{dt} - \frac{p_o}{\rho_o^2}\frac{\partial \rho}{\partial t} \tag{17}$$

The final equation required for the derivation is the equation of state. By considering the pressure as a function of the density and temperature, this can be written in its most general form as:

$$p - p_o = dp = \left(\frac{\partial p}{\partial \rho}\right)_T d\rho + \left(\frac{\partial p}{\partial T}\right) dT \tag{18}$$

$$= \left(\frac{\partial p}{\partial \rho}\right)_T \rho_o S + \left(\frac{\partial p}{\partial T}\right)_\rho dT$$

where p and p_o are analogous to ρ and ρ_o.

In order to obtain the absorption coefficient, the variables p, ρ, S, and T are assumed to vary harmonically, i.e., $\propto \exp[i(\vec{K}\cdot\vec{r} - \omega t)]$, and the propagation constant is assumed to be complex. For one dimensional motion, this reduces to

$$q = q_o e^{i(K_r x - \omega t)} e^{-\alpha x} \tag{19}$$

where q is the variable under consideration

q_o is the equilibrium value of q

K_r is the real part of the propagation constant

α is the imaginary part of the propagation constant.

Equation (19) indicates that the generalized variable q suffers a dissipation proportional to $e^{-\alpha x}$. The quantity α is the desired absorption coefficient and has units of cm^{-1}.

One further assumption which is true to a first order approximation and which facilitates the derivation a great deal is that all absorption mechanisms are independent of one another.[7] This allows the calculation of the absorption coefficient for each mechanism separately and then the overall coefficient is obtained by merely summing the individual components.

Now consider the system of equations given by Eqs. (4), (14), (17) and (18), first neglecting the heat conduction term in Eq. (18) and then neglecting the viscosity term in Eq. (14). Then the equations will be:

(4a) $$Ku - \omega S = 0$$

(14a) $$(\omega - i\frac{4}{3}\frac{\eta}{\rho_o}K^2)u - \frac{K}{\rho_o}p = 0$$

(17a) $$-\frac{p_o}{\rho_o}S + c_v\,dT = 0$$

(18a) $$-\left(\frac{\partial p}{\partial \rho}\right)_T \rho_o S + p - \left(\frac{\partial p}{\partial T}\right)_\rho dT = 0$$

and

(4b) $$Ku - \omega S = 0$$

(14b) $$\omega u - \frac{K}{\rho_o}p = 0$$

(17b) $$-\frac{p_o}{\rho_o}S + [c_v - \frac{i\kappa K^2}{\rho_o \omega}]dT = 0$$

(18b) $$-\left(\frac{\partial p}{\partial \rho}\right)_T \rho_o S + p - \left(\frac{\partial p}{\partial T}\right)_\rho dT = 0$$

In order for these equations to have solutions, the secular determinant must be set to zero in each case. After solving secular determinant, the solutions are

(20a) $$\frac{K^2}{\omega^2} = \frac{1}{C_o^2 + i\,\frac{4}{3}\,\frac{\eta}{\rho_o}\,\omega}$$

(20b) $$\frac{K^2}{\omega^2} = \frac{1}{C_o^2}\;\frac{1 - i\left(\frac{\kappa K^2}{\rho_o \omega c_v}\right)}{1 - i\left(\frac{\kappa K^2}{\rho_o \omega c_v}\right)\frac{\left(\frac{\partial P}{\partial \rho}\right)_T}{C_o^2}}$$

where K is the complex propagation constant and C_o is the unperturbed sound velocity.

To find α the imaginary parts of Eqs. (20a,b) are set equal. Then

(21a) $$2K_r\alpha = \frac{\left(\frac{4}{3}\right)\left(\frac{\eta}{\rho_o}\right)\omega^3}{C_o^4 + \frac{16}{9}\,\frac{\eta}{\rho_o^2}\,\omega^2}$$

(21b) $$2K_r\alpha = \frac{\omega^2}{C_o^2}\left(1 - \left(\frac{\partial P}{\partial \rho}\right)_T \frac{1}{C_o^2}\right)\left(\frac{\kappa K^2}{\rho_o \omega c_v}\right)$$

In both cases it is assumed that $K_r \simeq \omega/C_o$,[7] which implies that in Eq. (21a), the second term in the denominator can be neglected compared to the sound velocity term, i.e.

$$C_o^4 \gg \frac{16}{9}\,\frac{\eta}{\rho_o^2}\,\omega^2$$

In Eq. (21b), the K^2 on the right side is the complex propagation constant; however, this is usually also approximated by setting $K^2 = (\omega/C_o)^2$. With these approximations, the final expressions for the absorption coefficients are:

$$\alpha_{vis} = \frac{2}{3} \frac{\eta\omega^2}{\rho_o C_o^3} \tag{22a}$$

$$\alpha_{thermal} = \frac{\omega^2}{2c_v \rho_o C_o^3} \left[1 - \frac{1}{C_o^2} \left(\frac{\partial p}{\partial \rho}\right)_T\right] \tag{22b}$$

Using the thermodynamic relationship

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{1}{\gamma} \left(\frac{\partial p}{\partial \rho}\right)_S \equiv \frac{C_o^2}{\gamma} \tag{23}$$

where $\gamma \equiv c_p/c_v$,

the final value of the classical absorption coefficient becomes

$$\alpha = \frac{2\pi^2 \nu^2}{\rho C_o^3} \left[\frac{4}{3} \eta + \frac{(\gamma-1)\kappa}{c_p}\right] \tag{24}$$

where ν is the frequency (cps).

Using Eq. (24), the values of the absorption coefficient of liquid nitrogen and oxygen for various temperatures were calculated from the physical constants found in the literature. (Liquid nitrogen was used extensively in testing the apparatus.) Experimental values for the density, viscosity, and sound velocity were available for both liquid nitrogen and oxygen.[8,9] Also, the thermal conductivity of liquid nitrogen has been experimentally measured.[8] The ratios of specific heats were obtained from calculations done by Van Itterbeek and Van Dael.[10] These calculations were based on thermodynamic equations which relate the sound velocity, density, compressibility, and expansion coefficient to the specific heats. Tsederberg and Timrot[11] made extensive thermal conductivity measurements on liquid oxygen. From their data, they derived the empirical relationship,

$$\kappa = \kappa_o + (4.30 \times 10^{-8})\rho^{2.11} \tag{25}$$

where κ is the thermal conductivity at the temperature under consideration,

κ_o is the thermal conductivity of gaseous oxygen at one atmosphere (3.514×10^{-4} cal/cm.sec.),

ρ is the density at the temperature under consideration.

The values of the absorption coefficients and the associated physical constants are given in Tables I and II. Equation (25) was utilized to obtain the thermal conductivity values for liquid oxygen. Previous calculations[12] for the contribution of the thermal conductivity to sound absorption in liquid oxygen utilized Hamman's[13] values for the thermal conductivity. These values are 30% higher than those obtained by Tsederberg and Timrot. Since Tsederberg and Timrot's experiment was much more complete than Hamman's, their values were considered to be more valid.

TABLE I.

Classical Absorption Coefficients and Associated Physical Constants for Liquid Oxygen

Temp. (°K)	$\rho\left(\frac{gm}{cm^3}\right)$	$C_o\left(\frac{cm}{sec}\right)$	η(poise)	$\kappa\left(\frac{cal}{cm.sec.^oK}\right)$	γ	$\frac{\alpha}{\nu^2}$ (sec^2cm^{-1})
90	1.142	9.13×10^4	1.85×10^{-3}	3.572×10^{-4}	1.690	7.02×10^{-17}
85	1.167	9.50	2.15	3.696	1.689	6.88
80	1.191	9.90	2.45	3.887	1.687	6.69
75	1.215	10.3	2.85	4.002	1.678	6.64
70	1.239	10.68	3.50	4.253	1.663	7.01
65	1.263	11.03	4.30	4.306	1.645	7.47
60	1.280	11.33	5.75	4.414	1.621	8.86

TABLE II.

Classical Absorption Coefficients and Associated Physical Constants for Liquid Nitrogen

Temp. (°K)	$\rho\left(\frac{gm}{cm^3}\right)$	$C_o\left(\frac{cm}{sec}\right)$	η(poise)	$\kappa\left(\frac{cal}{cm.sec.^oK}\right)$	γ	$\frac{\alpha}{\nu^2}$ (sec^2cm^{-1})
76	0.815	8.68×10^4	1.65×10^{-3}	3.384×10^{-4}	1.877	10.36×10^{-17}
74	0.820	8.90	1.81	3.4580	1.838	10.24
72	0.831	9.08	2.00	3.5230	1.812	10.31
70	0.840	9.25	2.20	3.5870	1.783	10.39
68	0.850	9.45	2.40	3.6570	1.744	10.32
66	0.860	9.58	2.65	3.717	1.728	10.64

III. EXPERIMENTAL APPARATUS AND PROCEDURE

The equipment used in this experiment can be divided into two general categories. First, the cryogenic apparatus performed the task of bringing the liquid sample to and maintaining it at a given temperature. Second, a suitable mechanical system used in conjunction with pulse-echo type electronic apparatus was employed to obtain the sound absorption measurements. A photograph of the entire set-up is shown in Fig. 1.

A. Cryogenic Apparatus

1. Dewar and Magnet Arrangement

The triple neck dewar flask (Fig. 2) was especially designed to fit between the coil housings and pole pieces of the magnet. The magnet employed was a model 6A-HIA manufactured by The Pacific Electro-Motor Company and was powered by a model RC-3-3000-5-S power supply. With this combination, it is possible to obtain regulated magnetic fields up to 12 kG. The lower neck of the dewar was made to fit in the 2.5-inch gap between the pole pieces with less than 1/16-inch clearance. The middle neck is 4 inches in outside diameter and the upper neck has a 4-inch inside diameter. The dewar construction afforded the maximum possible volume (3.5 liters) commensurate with the magnet's dimensions, thereby allowing the liquid in the dewar to reach an equilibrium state even with such a large heat source as the ultrasonic measuring equipment immersed in it. The dewar is attached to a ten-inch square brass mounting plate with a conventional four-inch diameter aluminum mounting ring and gasket. The brass plate is securely fastened to a Dexion steel frame (shown in Fig. 2) which positions the dewar between the pole pieces. The entire frame is covered with half-inch plywood which was put on as a safety precaution in the event of dewar failure.

Figure 1 - Experimental Setup

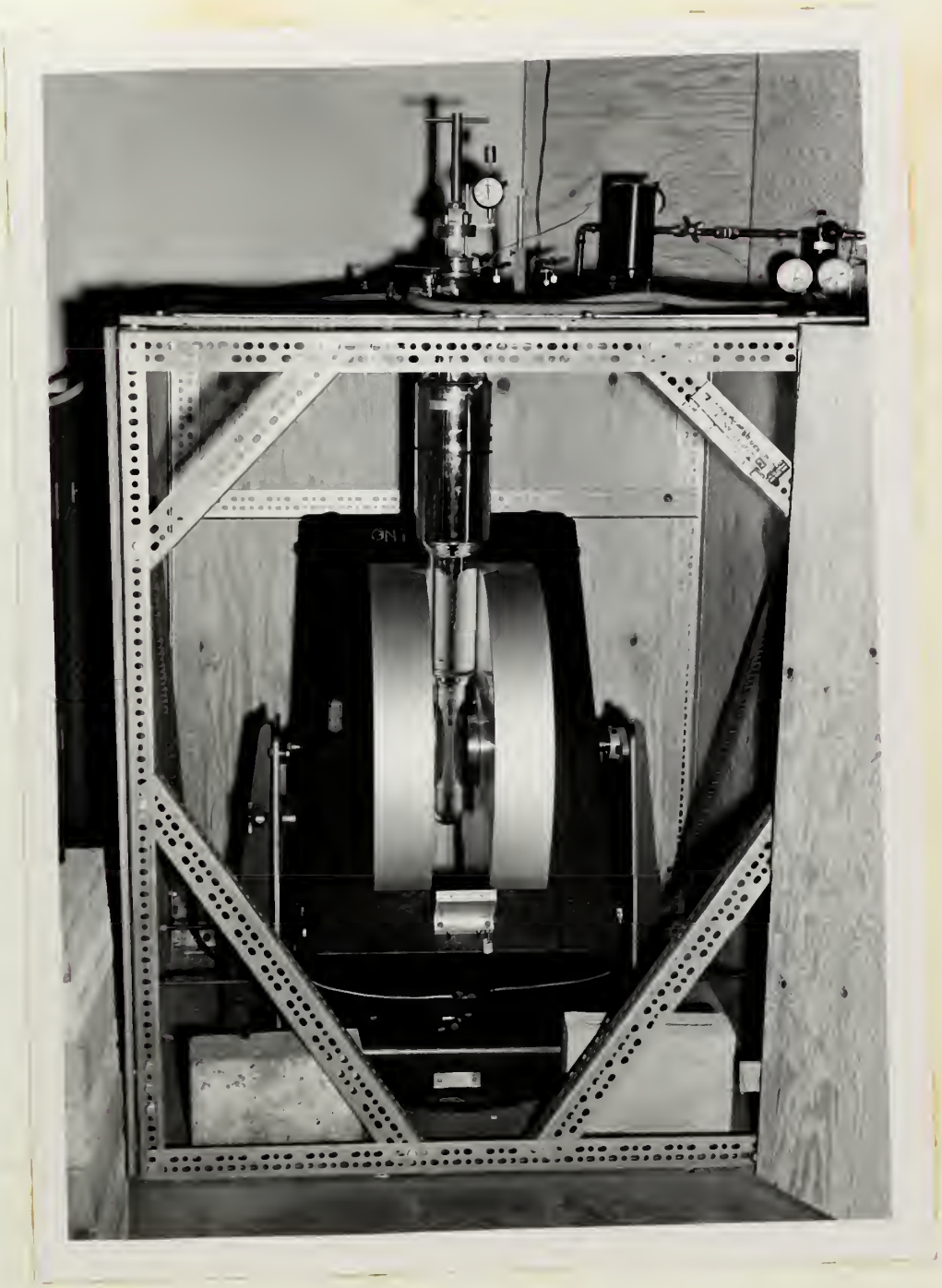

Figure 2 - Triple Neck Dewar

2. Sample Chamber

The sample chamber (Fig. 3) is inserted into the dewar through the top of the mounting plate and is sealed with a neoprene rubber O-ring and screwed to the mounting plate. The sample chamber consists of the cap, which contains the attachments for the fill and pump lines, a condenser coil, and a 1 7/8-inch outside diameter tube. The tube is made of 0.012-inch thick stainless steel from the top of the cap down to the bottom of the condenser coil. The remainder of the tube is made of 1/8-inch thick copper. The reason for this construction is twofold. First, in order to minimize thermal conduction from the cap, which is at room temperature, a material with poor heat conductivity had to be used. Obviously, the thinnest tube commensurate with strength considerations enhances this effect. Second, in the sample region, it is desirable to have an isothermal bath free of temperature gradients to preclude erroneous measurements. This is accomplished by surrounding the sample with a reasonably heavy, highly thermal conducting metal.

3. Manostat

Protruding from the sample chamber cap are connections for filling the dewar and sample chamber and also a 5/8-inch outside diameter pipe leading to the pumping line. This pipe leads to the manostat which is a device used to maintain a constant vapor pressure over the liquid in the dewar. The operation of the manostat will be described with the aid of Fig. 4.

The connections to the dewar and the vacuum pump are made through the intake port A and the exhaust port B, respectively. The pumping rate of the system is regulated by the coarse control valve C and the orifice screw D. The orifice screw controls the vertical position of the orifice E inside the manostat chamber. (The manostat is supplied with three orifices which are

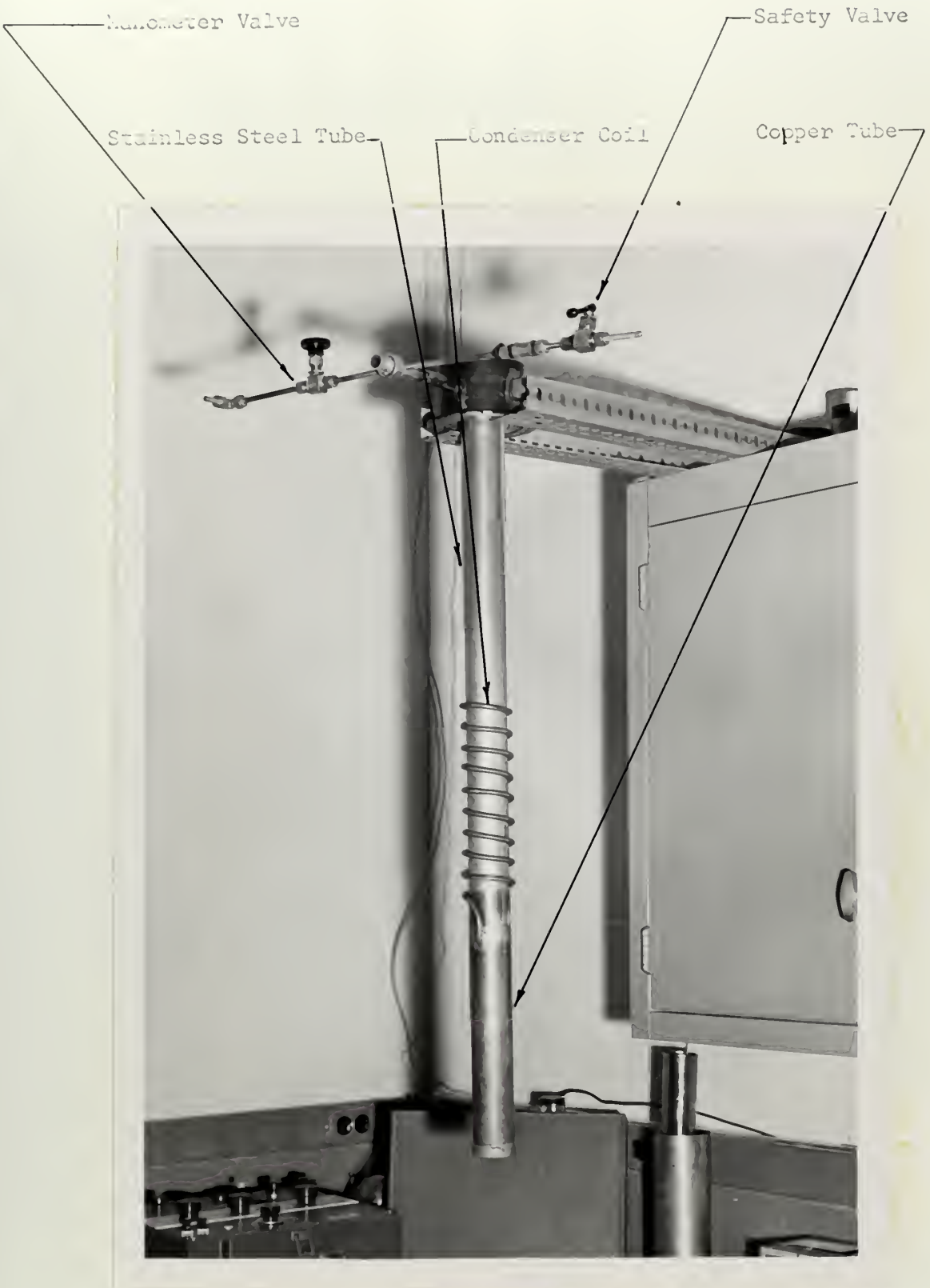

Figure 3 - Sample Chamber

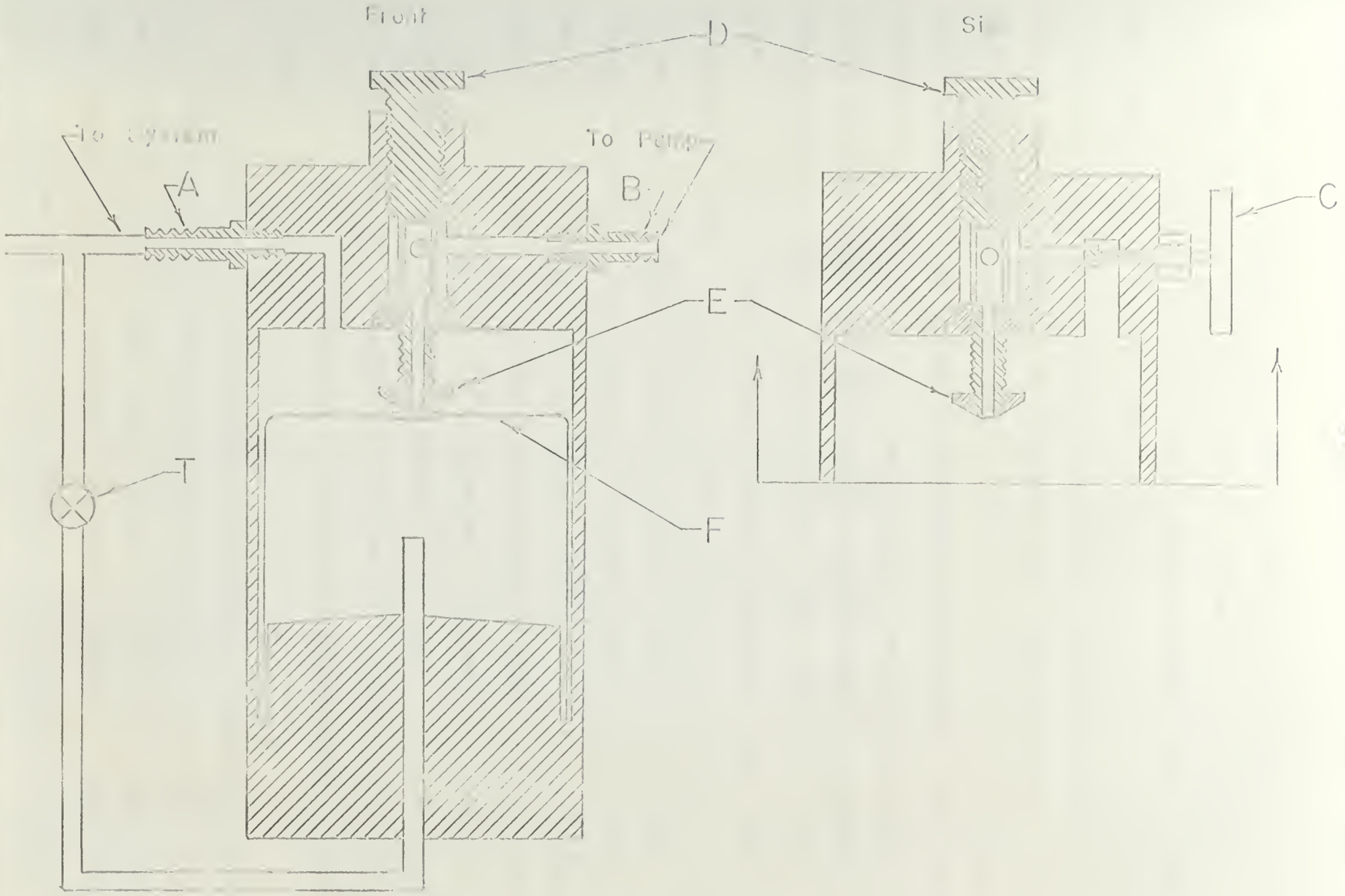

Figure 4 Schematic of Manostat

1, 2, and 4 mm in diameter. The largest was used in this experiment in order to provide the best pumping rate possible.) The orifice seats against a small rubber diaphragm which is on top of the thin aluminum float F. The float, which is cylindrical in shape and open at one end, rests inverted in a 15-ml mercury reservoir which is at the bottom of the inside chamber. In order to obtain a particular vapor pressure in the dewar, the valve C is first fully opened and the orifice E is set at a position which is approximately three-quarters of the way to its lowest point of travel. Also, the toggle valve T should be in the closed position. Now the vacuum pump is turned on and as the pressure approaches the desired value (as indicated on the manometer), the valve C is slowly closed. When this valve is fully closed, the pressure should be approximately at the desired value. Finer adjustment (to within ±1 mm Hg) can be attained by moving the orifice E up or down depending on whether a further decrease or increase in the vapor pressure is required. The pressure in the chamber above the float is the same as that of the system while atmospheric pressure exists in the chamber underneath the float. If the system pressure becomes higher than that set with the manostat, the float will be depressed. This unseats the orifice which allows the pump to reduce the pressure in the dewar. Once the desired pressure is regained, the diaphragm on the float will re-seat itself against the orifice. With this arrangement the pressure can be maintained to within ±1 mm Hg.

The manostat used in this experiment was modified by inserting a 1/4-inch o.d. stainless steel tube through the bottom of the outer can and into the chamber covered by the aluminum float. The other end of the tube was connected to the toggle valve T and then to the system side of the manostat (see Fig. 4). This was done so that the sensitivity of the instrument could be

retained at any value of system pressure. If the pressure differential between the upper and lower chambers which are separated by the aluminum float becomes greater than one atmosphere, the rubber diaphragm will be permanently seated against the orifice and no control is possible. Control can be regained for very low pressures (less than 1 mm Hg) by equalizing the pressure in the two chambers at some arbitrary value (usually around 1 mm Hg). The equalization is effected by opening the toggle valve which allows the system pressure in both the upper and lower chambers. After this is done, the toggle valve is again closed and the new reference pressure exists in the lower chamber. When the apparatus is shut down completely, the toggle valve T is normally left open.

4. Vacuum Pump

In any system which contains oxygen, precautions have to be taken to ensure that no oil, grease, and dirt are present on any component with which the oxygen might come in contact. This is particularly important when it is desired to pump on oxygen. Using an ordinary hydrocarbon based oil in a vacuum pump which is pumping on oxygen is extremely hazardous because when such an oil is exposed to an oxygen atmosphere, the combustability of the oil is greatly enhanced; thus, leading to the possibility of a fire or even an explosion. To avert this, the vacuum pump used had to be modified with seals and gaskets which were compatible with the oil used in the pump. The oil used has the trade name Cellelube 100. Another commercially available oil sometimes used is tricresyl phosphate. The pump employed was a Model 1405 Welch Duo-Seal vacuum pump which is capable of obtaining an ultimate pressure of 1×10^{-4} mm Hg and has a pumping rate of 54 liters per minute at atmospheric pressure.

5. Valve Arrangement

The various valves have been given letter designations in the block diagram, Fig. 5. The use of these valves is as follows:

1. Valves A and B. These two valves control the exhaust from the dewar. While filling the dewar, valve B is closed so that the manostat is not subjected to the very high overpressure from the storage tank. Valve A is opened during filling and the exhaust is vented into the room. Of course, when pumping, valve B is open, and valve A is closed.

2. Valves E and F. These two valves control the pressure on the system side of the pump. Sometimes it is desirable to maintain a vacuum in the system when the pump is not operating. When this is done, the oil in the pump will back up into the system unless the pressure is equalized at the pump. In order to do this, valve E is first closed to hold the vacuum in the system; then valve F is opened to allow atmospheric pressure in the pump line. The amount of vacuum on the pump is roughly indicated on the dial gauge indicated in Fig. 5. With both valves open, this combination also can serve as an exhaust station.

3. Valve G controls the manometer. This valve must be closed while filling the dewar, and is normally not opened until after the pump has been turned on and a definite vacuum is indicated on the dial gauge.

4. Valve H controls access to the condenser coil and is normally open only when filling the sample chamber.

5. Valve S is the safety valve. It is actuated when one pound over pressure exists in the system.

6. Valves C, D and T are used to operate the manostat as described above.

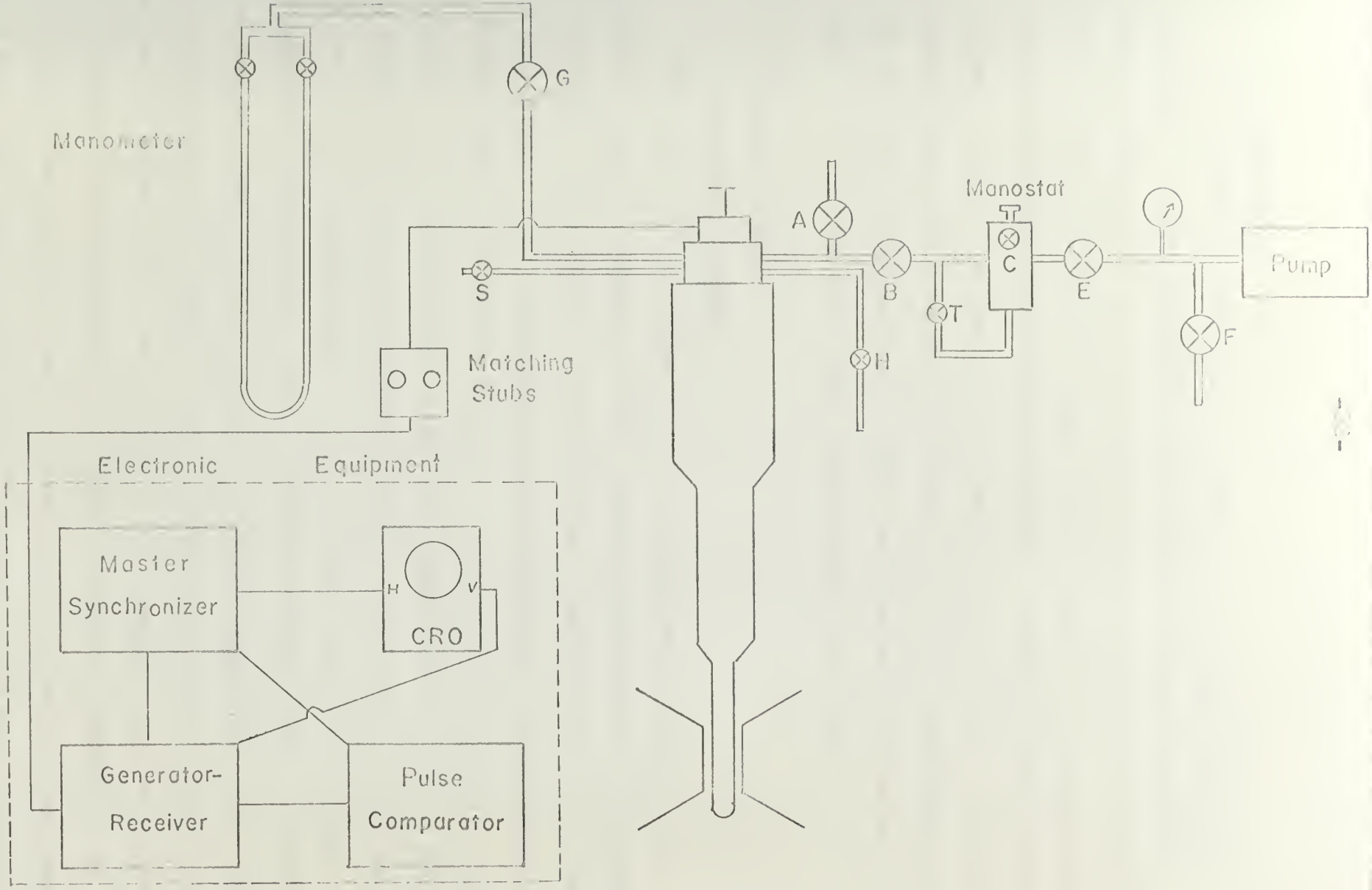

Figure 5 Block Diagram of System

6. Thermocouple

The temperature at the sample was measured with a copper-constantan thermocouple. A Leeds and Northrup Model 8686 potentiometer was used to obtain the thermocouple emf's. The emf's were converted with tables made up from the measurements of Powell, Bunch, and Corruccini.[14] The thermocouple was made by a heliarc weld, calibrated by using the boiling points on liquid nitrogen and oxygen, and used with a reference junction of 0°C. In the temperature range of liquid nitrogen, the sensitivity of the thermocouple ranges from 13 to 18 μV per degree Kelvin. Since the potentiometer can be read to within ±2 μV, the temperature could be measured to within ±0.2°K.

B. Ultrasonic Apparatus

1. Electronic Equipment

With the electronic equipment used in the pulse-echo technique it is possible to use the transducer as both transmitter and receiver of the ultrasonic signal. The transmitted signal which has a maximum duration of 5 μsec in the equipment used, is propagated into the sample and is reflected by a reflector which must be exactly parallel to the transducer and which is optically flat. The reflector must satisfy these requirements in order to obtain an undistorted signal in the reception pattern. During the receiving portion of the cycle, the original signal will be reflected back and forth between transducer and reflector many times. During each passage through the sample, the original signal will be dissipated by an amount proportional to the absorption coefficient of the sample. Also, only part of the signal will be reflected at each reflecting surface, the remainder being transmitted into the reflector or transducer as the case may be. The reception pattern is observed on an oscilloscope and consists of series of equally spaced pulses with each successive pulse being smaller in amplitude. The envelope of the wave train must be

an exponential curve in accordance with Eq. (19).

The equipment used to generate, receive, and display the ultrasonic signal consists of four major components (see Figs. 5 and 6). The system centers around the r.f. pulse generator and receiver unit, Matec model 560. This unit is capable of generating frequencies in the range 10 - 310 MHz and has a continuously variable pulse width from 0.5 - 5 μsec. The generated pulse is coupled to the transducer via the high impedance output terminal on the unit through a pair of impedance matching stubs. At the lower frequencies a peak-to-peak voltage of approximately 1000 volts is available at the output terminal. In the receiver portion of the unit, the echos of the reception pattern are first converted to 60 MHz; then amplified in the I. F. amplifier. The I. F. frequency is filtered out after the echos are amplified and detected. Following detection the output impedance is lowered by means of a cathode follower circuit so that the received signals can be coupled to an oscilloscope via a coaxial cable. In addition to the oscilloscope, the Matec Model 120 Master Synchronizer and the Matec Model 666 comparison pulse source are connected to the generator-receiver unit.

The comparator pulse source generates an electronic pulse which has the same waveform as the echos in the reception pattern. This pulse is also displayed on the oscilloscope and its amplitude can be varied with the step-type potentiometers on the comparator source unit. The potentiometers are calibrated directly in decibels with a range of 0 - 60 dB at intervals of 0.1 dB.

In order to allow alternate oscilloscope display of the comparator pulse and the reception pattern, a source of triggering pulses with a suitable timing sequence must be employed. These triggering pulses are generated by the master synchronizer unit. Briefly, the operation of the unit is as follows. The synchronizer unit triggers the oscilloscope at finite intervals of t_o, t_1, t_2,

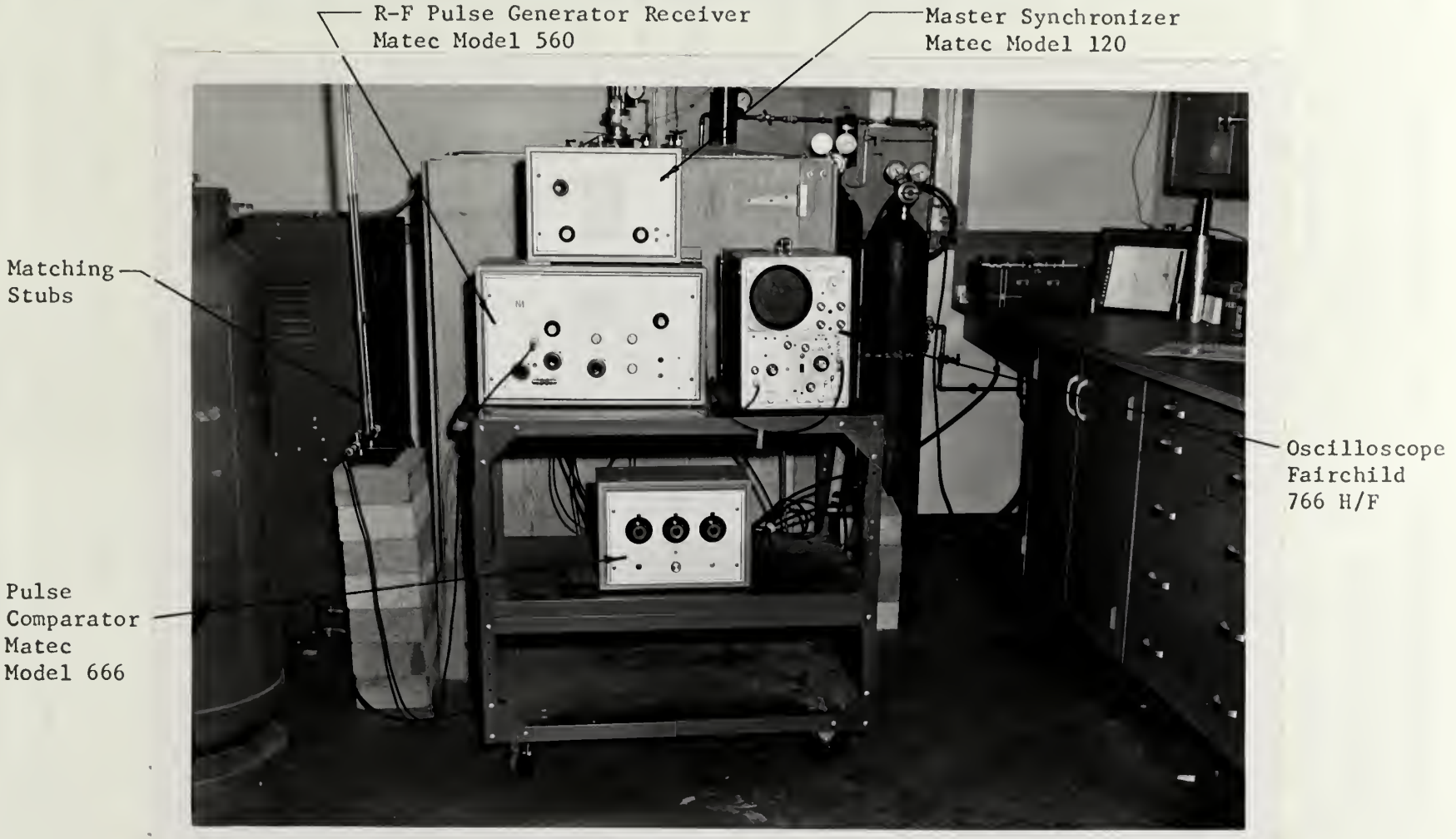

Figure 6 - Electronic Equipment

etc., where the triggering interval is at half the basic repetition rate. Also, the r-f generator is triggered at times t_o, t_2, t_4, etc., and the pulse comparator is triggered at $(t_1 + \tau)$, $(t_3 + \tau)$, etc., where τ is between 0 - 1000 μsec. This alternating triggering sequence provides the alternate display desired. Because of the persistence of the oscilloscope screen, the two signals appear as if they are superimposed; consequently, the comparator pulse can be used to measure the echo amplitudes in the reception pattern. A time delay generator is also incorporated in the master synchronizer unit. It has three calibrated ranges of 0 - 10, 0 - 100, and 0 - 1000 μsec. The time delay generator enables one to measure the relative time difference between successive pulses in the wave train; thus, velocity measurements can be made to within 1%. A more thorough circuit analysis of this system is available in the literature.[15]

2. Mechanical Equipment

The mechanical setup used was patterned after the one used by Chase in his liquid helium measurements.[1] Description of the unit will be made with the aid of Figs. 7 and 8. On the cap there are three paralleling screws, A, A', A", which are mounted on a movable plate B which is in turn threaded onto the master screw C. The two paralleling screws A and A' have 80 threads per inch while the third has 50 threads per inch. By turning the master screw, the movable plate moves vertically and is guided by the T-block D. Extending from the side of the plate is a flat brass bar E on which is mounted the spring loaded pin of a precision dial gauge (see Fig. 8). The dial gauge used was a Starret Precision dial gauge, model 25-881, which had a range of 25 mm and could be read to within ±0.01 mm.

Suspended from the cap are three equally spaced quartz tubes G (5-mm o.d. and 2-mm bore) which are kept in line with three plexiglass spacers. The

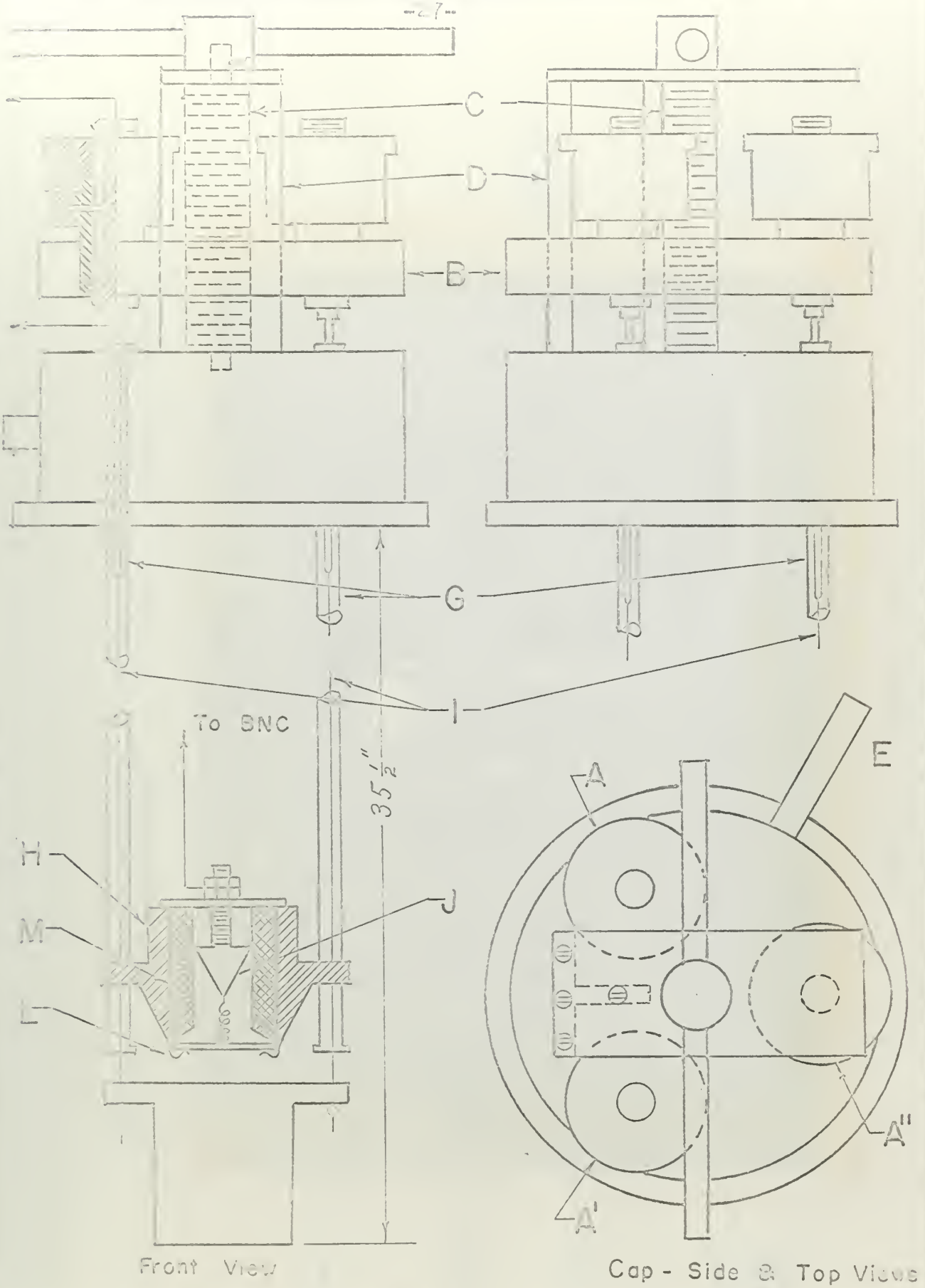

Figure 7 Mechanical Unit

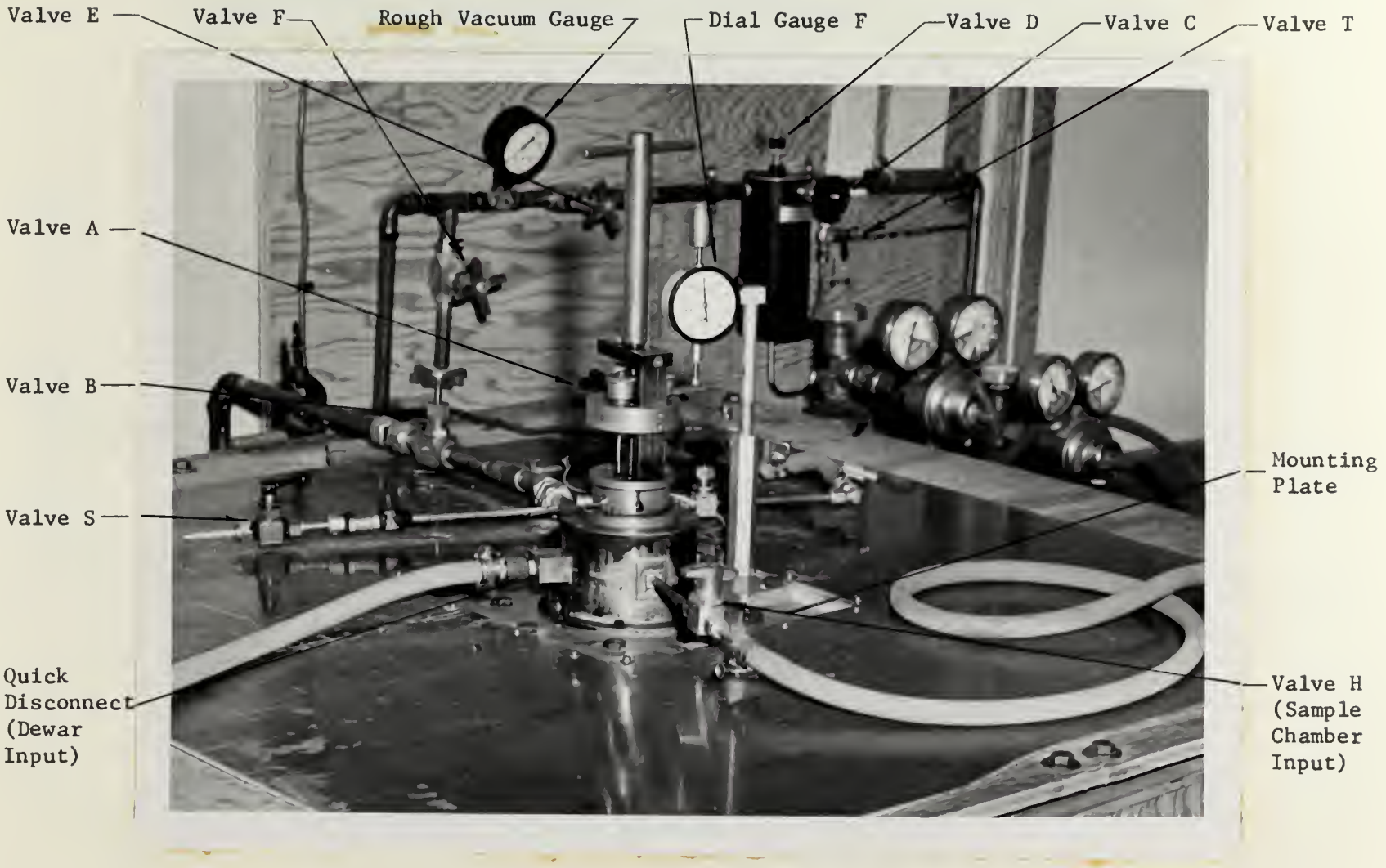

Figure 8 - Closeup of Cap Area

Figure 9 - Mechanical Unit

transducer housing H is attached to the bottom of the tubes by means of teflon tipped brass screws while the reflector suspension wires I pass through the center of the tubes. Quartz was used to minimize distortion of the tubes due to thermal contraction. In addition to the schematic, this arrangement is also shown in the photograph, Fig. 9.

The transducer housing H was one of the most troublesome areas in the entire experimental setup. In most ultrasonic equipment, it is advantageous to have as large a mismatch as possible between the specific acoustic impedance on either side of the transducer. If the specific acoustic impedance behind the transducer is much less than that of the sample, almost all of the acoustic energy generated will be propagated into the sample. Therefore, if the sample is a liquid or a solid, an excellent backing material would be air or even a vacuum. Air backing could not be used in this experiment, however, since the unit is operated at temperatures below the boiling points of nitrogen and oxygen -- the principal ingredients of air. This liquefaction of air would lead to contamination of the sample and also gives the condition of a symmetrically loaded transducer. The former condition was unacceptable; consequently, holes were drilled in the housing to allow the sample liquid in behind the transducer. With a transducer which is symmetrically loaded an equal amount of acoustical energy is transmitted in each direction; therefore, half of the useful energy is lost. The situation is further complicated by the echos which return to the backside of the transducer after being reflected from some portion of the transducer housing. These echos interfere with the desired reception pattern; consequently, the observed signal is highly distorted and unusable. In order to remedy this situation, a cone shaped electrode J was adopted to disperse the backward transmitted signal. Contact between the electrode and the transducer is made with a very thin copper-

beryllium spring (0.010-inch diameter wire). The opposite end of the electrode is connected to a co-axial cable which, in turn, leads to the BNC connector on the side of the cap. An RG-196 U co-axial cable was used because of its thinness which minimized heat conduction from the cap area. The backside of the transducer could have been evacuated or filled with a gas such as helium in order to obtain a greater amount of useful energy; however, since the signal obtained with the symmetrically loaded crystal was very strong, it was felt that the increased experimental difficulties were not justified.

The transducer used was a one-inch diameter, X-cut quartz crystal with a fundamental resonance frequency of 10 MHz. The face which was in contact with the sample was completely gold plated, while the opposite side was plated out to 3/4 of an inch in diameter. The crystal is held in place with three equally spaced copper-beryllium leaf springs L which also serve as the ground connection between the housing and the crystal. The cone shaped electrode is insulated from the transducer housing by means of a teflon insert M. The bottom of this insert as well as the side of the housing itself were beveled in order to avoid extraneous signals in the reception pattern.

The reflector is made of solid brass and is suspended by three 0.005-inch diameter copper beryllium wires which pass through the quartz tubes and are soldered to shafts which extend from the paralleling screws into the tubes. The screws are made in such a way that when turned for adjustment, the shafts do not rotate but travel longitudinally in the tubes; therefore, preventing the twisting of the wires (see cross section in Fig. 7). Copper-beryllium wire was used because this material is extremely strong while at the same time being very ductile; thus, allowing the wire to be drawn down to a

0.005-inch diameter. Such a thin wire is necessary to minimize heat conduction from the cap area which could possibly induce boiling. In order to reduce the pendulum effect of the reflector, each quartz tube was capped with a small brass plug with a 0.010-inch diameter hole drilled through the center. The wires were threaded through these caps and then attached to the reflector. The reflector movement is accomplished by turning the master screw which, in turn, raises or lowers the movable plate. Since the plate and the reflector move together, the amount of reflector movement is obtained by measuring the plate movement. This was done with the precision dial gauge described above.

The choice of materials used for the construction of the transducer housing and the reflector was somewhat restricted by the fact that the equipment was to be subjected to a strong magnetic field. Stainless steel would have been preferable from the standpoint of corrosion; however, even the so-called non-magnetic type 304 stainless steel was affected by a field of 5000 gauss. Quartz would have been an excellent choice for reflector material; however, in this case it was felt that the additional weight gained by using brass (density 8.50 vs. 1.28 gm/cm^3) plus the increase in the reflection coefficient (0.93 vs. 0.74); brass was the better material. A heavy reflector was needed to keep the wires taut. The bottom face of the reflector has a spiral groove machined into it to disperse reflections from that surface.

C. Experimental Procedure

1. Pulse-echo techniques

There are three methods available to measure sound absorption in liquids utilizing the pulse-echo technique. In many of the pulse-echo electronic systems an exponential curve generator is incorporated which allows the display of a continuously variable exponential curve simultaneously with the reception pattern. The attenuation coefficient can be determined by matching

the exponential curve to the received wave train for a series of different transducer-reflector distances. The readings obtained from the exponential generator are converted to dB/μsec using a calibration curve supplied with the unit. Also, for each set of measurements a velocity measurement is made; then each reading can be converted to dB/cm. An error inherent in this method arises from the fact that the sound is not only absorbed in the sample, but also at the transducer and reflector at each reflection. In order to correct for this, a plot of dB/cm versus the reciprocal of the transducer-reflector distances used is made for each set of data. This plot should be a straight line, and when this line is extrapolated to $1/x = 0$, the value of α in dB/cm obtained at that point should be the true value of the absorption coefficient.

A second method which utilizes the exponential curve requires that the mechanical arrangement maintain reflector-transducer parallelism while the two are continuously separated. The procedure in this case is to match one of the pulses of the wave train, usually the first, to the exponential curve. As the reflector and transducer are separated, the shape of the exponential curve is continuously changed with the control knob on the exponential generator. There will be one curve which the selected pulse follows exactly as the transducer-reflector distance is changed. Once this curve is found, the absorption coefficient is known.

The last method available utilizes the comparator pulse unit which was described previously. The exact procedure involved in this method will be explained in detail later; however, it should be noted why this method was the only one which was used with this system. In the exponential method, the absolute reflector-transducer distance must be accurately known. The system employed here was designed to give accurate relative distance measurement only.

In order to be able to use the second method, parallelism must be maintained throughout the movement. Since in this unit the reflector is suspended by wires, the small pendulum effect which is present precluded exact parallel movement; hence, the reflector had to be re-aligned at each position. Even if these limitations were not present, it is felt that the comparator pulse method is the most accurate since the measurements are made directly in decibels to within ±0.1 dB, and if only the first pulse is used at each distance position, the reflection losses do not affect the measurement.

2. Sample Preparation

Much of the experimental procedure deals with preparing the liquid sample for measurement. In order to avert undue thermal shock to any part of the system, the mechanical unit was inserted into the sample chamber which in turn was inserted into the dewar prior to introducing any cryogenic fluids. Once the system was filled with the desired combination of fluids, it was necessary to wait about 30 minutes in order for the system to reach an equilibrium state. This facilitated pumping on the system when lower vapor pressures were desired. Once the desired vapor pressure for a given temperature was obtained, another 15 - 30 minutes were required before equilibrium was attained, the amount of time depending on the temperature change involved.

The type of liquid used in the dewar was dictated by the temperature range of the measurements to be made. Nitrogen is in its liquid phase from 63.4 - 77.3°K, while for oxygen the range is 53.4 - 90.13°K. Consequently, liquid nitrogen was used in the dewar to make the measurements on oxygen at 65°, 70°, and 75°K. Obviously, this procedure is inherently safer than pumping on oxygen and also time was saved, since less of a vapor pressure reduction was required when bringing liquid nitrogen down to these temperatures than would be required to bring liquid oxygen down to the corresponding range.

Before any cryogenic fluid was put into the system, both the dewar and sample chamber were purged with gaseous oxygen or nitrogen, whichever was appropriate. Both the gas and the liquid were put into the dewar through the "quick-disconnect" connection shown in Fig. 8, and for the sample chamber; through valve H, Fig. 5. The lines used to transfer oxygen and nitrogen from the storage dewar were merely gum rubber hose #133 manufactured by Green Rubber Co. The storage dewars used were the LS-160 and LS-110 storage tanks manufactured by the Linde Corporation. The former was used for liquid nitrogen while the latter, for liquid oxygen; and they have a capacity of 160 and 110 liters, respectively (see Fig. 1). Using these tanks automatically ensured sample purity, for the tanks were overpressured with the boil-off vapor from the liquid inside. Overpressure safety valves released at 200 psi. Liquid transfer was particularly simple with this arrangement, for the fluid was forced through the withdrawal valve by the overpressure existing in the tank. This eliminated the more cumbersome procedure of over-pressurizing the storage tank from a separate source. The Linde Corporation guaranteed the purity of the liquid and gaseous nitrogen to be better than 99.7%, the liquid and gaseous oxygen to be better than 99.5%.

When liquid nitrogen was being transferred into the dewar, oxygen or nitrogen gas was fed into the sample chamber through the condenser coil. In the case of the nitrogen-oxygen combination, the oxygen gas was very easily condensed while passing through the coil. For the nitrogen-nitrogen or oxygen-oxygen combination, the condensing procedure did not work as well. Pumping on the liquid in the dewar lowered the temperature enough for condensation to take place very slowly; therefore it was usually more expeditious to fill the sample chamber directly in these two cases.

The dewar was usually filled almost to the top of the silvered portion,

while the sample chamber was filled just enough to cover the transducer housing. This was done to yield a minimum temperature gradient in the region of the sample fluid, thus reducing the possibility of boiling of the sample. The level of the fluid in the dewar could be seen through a slit in the silvered glass. The level in the sample chamber was determined by observing the pattern on the oscilloscope. There is a very marked difference in the patterns in gas and liquid so that the transition was easily detected. Admittedly a more definite method of level indication would be desirable.

Once the dewar and sample chamber were filled, and the system reached a reasonable state of equilibrium as indicated by the absence of violent boiling in the dewar, the vapor pressure was reduced to correspond to the desired temperature for measurement. The values of vapor pressures and many other physical properties of cryogenic fluids are contained in the U. S. Department of Commerce Publication, PB 171 61B.[8] As the appropriate vapor pressure was reached, the manostat was set as described previously and the actual temperature in the area of the transducer and reflector was measured with the copper-constantan thermocouple. Because of the poor thermal conductivity of the substances used, the temperature at the sample as indicated by the thermocouple did not always coincide with that indicated by the vapor pressure. This discrepancy increased as the vapor pressure was reduced. This did not cause any great difficulty since the sample temperatures were always consistent at a given vapor pressure and did not change during the entire time which the measurements were taken.

3. Measurements

To make the absorption measurements, the dial gauge was set to 24 on the index. Next, the reflector was paralleled using a 10 MHz signal since this was a very strong signal with many echos. The desired pattern is one in

which there is a relative minimum between successive peaks in the wave train and where all the peaks rise to a maximum collectively as the paralleling screws are adjusted. The result should be an exponential curve. Unfortunately, in the electronic equipment used, an exponential decay curve is not superimposed on the wave train. However, by tuning the signal as described and then checking it on a pulse-echo unit which does have an exponential curve, an exponential pattern was usually obtained. A typical pattern is shown in Fig. 10.

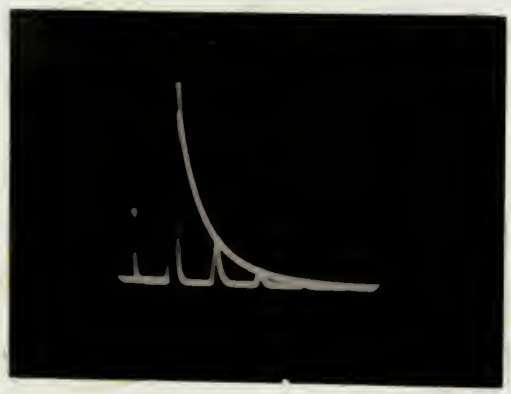

Figure 10. Liquid Nitrogen 74°K

Once the reflector is parallel, a 50 MHz signal is tuned with the aid of tuning stubs. A 50 MHz signal was used since this was the lowest frequency at which there was a measurable amount of absorption. Next, the comparator pulse on the oscilloscope is positioned next to the first pulse in the reception pattern and its amplitude is made to coincide to that of the first pulse. A convenient setting on the comparator unit is used as reference (usually between 25 - 30 dB); then, using the master screw, the reflector is moved further away from the transducer. Once in its new position the signal is again tuned for a maximum, and the comparator pulse is again matched to the first echo in the reception pattern. The amplitude of the comparator pulse

will have to be reduced by an amount equal to the relative absorption between the two positions. This procedure is repeated for a predetermined number of distance settings; then, a plot is made of relative absorption vs. distance. This is a straight line and its slope is the absorption coefficient in dB/cm.

In this experiment, a total of twelve successive distance settings at 2-mm intervals was used. Measurements were taken both for upward and downward reflector travel, and a velocity measurement was usually taken for each set of runs. The velocity was measured by measuring the time difference between the first and second pulse at the reference position and then again when the distance was changed by 18 - 20 mm. Both the relative change in distance and time could be measured very accurately ($\pm$0.01 mm and $\pm$0.5 μsec, respectively); therefore, this led to velocity measurements to within an accuracy of $\pm$1%. When liquid oxygen was used, every third run was made with a magnetic field of 10 kG imposed on the sample. Each run took approximately 30 - 45 minutes since the reflector had to be paralleled at every setting.

4. Safety

Safety was of paramount importance in the design and use of this equipment. There are a number of excellent publications which deal with the handling of liquid oxygen in particular and cryogenic fluids in general.[16,17,18] Many tragic examples of carelessness are contained in this literature, most of which could have been prevented by safety procedures which are very simple and require little extra effort.

Although some of these items have already been mentioned, a brief list of the safety practices in this experiment are listed below.

1. Use of proper oil in vacuum pump (Cellelube 100).
2. Cleanliness of all equipment.

3. Use of fan to circulate exhaust from the system while filling the dewar and also to circulate exhaust from pump.
4. Wood enclosure for dewar.
5. Metal plate on top of wood for top surface of enclosure. This was done since it has occurred in the past that wood saturated with oxygen will spontaneously ignite.
6. Safety valve leading to dewar which would release at an overpressure of one psi. This valve was incorporated in the event that the normal exhaust valves were inadvertently left closed. The sample chamber did not require this since it was always at atmospheric pressure.

IV. EXPERIMENTAL RESULTS

A. Velocity and Absorption Values

The results of the measurements made are tabulated in Tables III and IV. The absorption coefficients were obtained by first fitting the data to a straight line curve by the least squares method, and then computing the average slope of all the lines obtained. The velocity measurements agree with Van Itterbeek's values to within 3% as do Galt's; however, there is a considerable discrepancy between the absorption values.* Galt's results show no temperature dependence for absorption in liquid oxygen whereas a slight dependence was obtained in this experiment. The trend of this temperature dependence is generally the same as that predicted by the values computed from classical theory, although the experimental values are about twice as large. This is shown in Fig. 11. The experiment indicated rather conclusively that there is no magnetic field dependence on the absorption in liquid oxygen, for all the values obtained fluctuated about the zero-field value. Their difference (within 4%) was less than the estimated error of the experiment.

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*Van Itterbeek's values are used as a reference since his equipment was specifically designed to make velocity measurements.

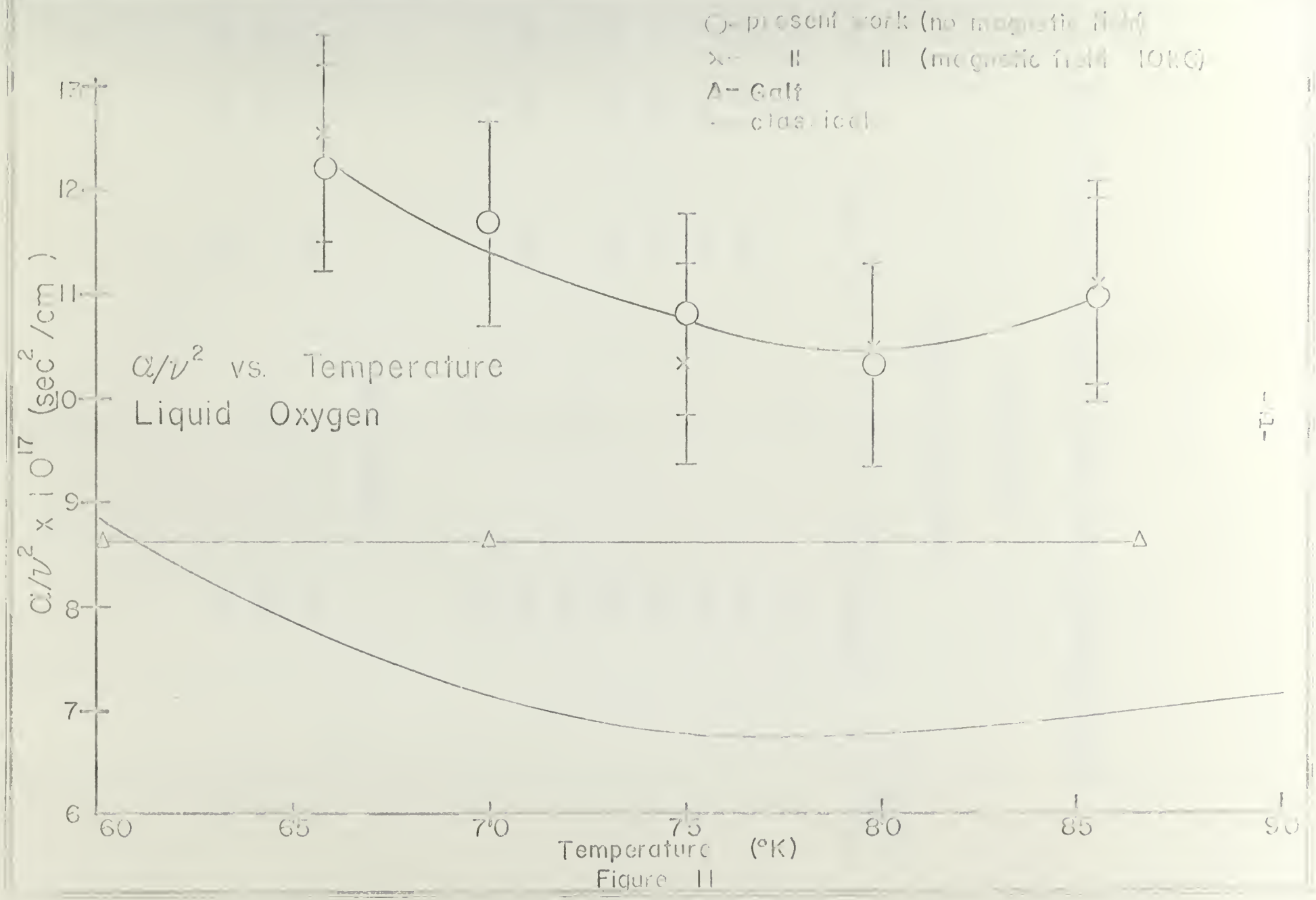

○- present work (no magnetic field)
×- " " (magnetic field 10KG)
Δ- Galt
- classical
α/ν^2 vs. Temperature
Liquid Oxygen
$\alpha/\nu^2 \times 10^{17}$ (sec^2/cm)
13
12
11
10
9
8
7
6
60
65
70
75
80
85
90
Temperature (°K)

Figure 11

TABLE III.

Sound Velocity Measurements in Liquid Oxygen and Liquid Nitrogen

Liquid Oxygen

Velocity ($\times 10^4$ cm/sec)

Temp. (°K)	Present Work	Galt's[5]	Van Itterbeek's[9]	% difference from Van Itterbeek
87.0 ± 0.2		952	970	1.8
86.1 ± 0.2	936		943	0.7
80.1 ± 0.2	981		990	1.0
75.4 ± 0.2	998		1030	3.1
70.2 ± 0.2	1030		1068	3.5
70 ± 1		1094	1068	2.5
66.3 ± 0.2	1062		1095	3
60 ± 5		1119	1133	1.2

Liquid Nitrogen

74.1 ± 0.2	895		890	0.6
73.9 ± 0.2		962	890	8.0
70.2 ± 0.2	934		925	1.2

TABLE IV.

Sound Absorption Measurements in Liquid Oxygen and Liquid Nitrogen

Liquid Oxygen

$\frac{\alpha}{\nu^2} \times 10^{17}$ ($sec^2 cm^{-1}$)

Temp. (°K)	No Mag. Field	Magnetic Field of 10,000 Gauss	Galt's
87.0 ± 0.2			8.6
86.1 ± 0.2	11.0	11.1	
80.1 ± 0.2	10.3	10.5	
77.3 ± 0.2	11.1		
75.4 ± 0.2	10.8	10.3	
70.2 ± 0.2	11.6		8.6
66.3 ± 0.2	12.2	12.5	
60.0 ± 5.0			8.6

Liquid Nitrogen

75.3 ± 0.2	13.1		
73.9 ± 0.2			10.6
70.2 ± 0.2	14.5		

B. Errors

There were two predominant sources of error in the apparatus. First, any vibrations from the floor were transmitted through the Dexion frame and then through the reflector suspension wires. This induced an oscillation of the reflector which in turn caused a jittery reception pattern. The greater the transducer-reflector distance, the more the vibrations affected the signal. At the lower end of the reflector travel, this caused an error in reading the comparator pulse ±0.2 dB.

A more serious error was induced by the fact that parallelism of the reflector had to be adjusted at each reading. As was mentioned previously, the fine paralleling controls had 80 threads per inch, and the coarse control, 50 threads per inch. Since adjustment of the paralleling screws moved the edge of the reflector, the center to center distance between the reflector and transducer was changed half as much. The average adjustment which had to be made was about one-half a turn which corresponds to a change of ±0.08 mm and ±0.13 mm in the center to center distance for the fine and coarse controls, respectively. Since the transducer-reflector distance was changed by 2 mm for each reading, an error in the path length of ±7% could be introduced by adjusting the coarse knob. Assuming that on the average, the attenuation could be measured to within ±0.1 dB, and using the fact that for oxygen the average attenuation measurement was 1.0 dB for 4 mm of path length, each measurement would have an error of ±15%.

The above analysis is for the worst possible situation. The error in path length was averaged out over a distance change of 18 - 20 mm as is indicated by velocity measurements. Using Van Itterbeek's sound velocity values, the average error in path length is estimated to be ±3%. Using this value, the average error in the overall absorption measurements is estimated

to be ±10%.

Another source of error could originate from the presence of temperature gradients. Although the observed wave trains did not exhibit the typical oscillation which usually accompanies this phenomenon, the fact that the thermocouple and vapor pressure temperatures did not always coincide might indicate the presence of such a discrepancy. Possibly, part of the oscillations believed to be caused by vibrations were really caused by temperature inhomogeneity; however, the oscillations did have a much shorter period than would normally be expected from temperature gradients. Of course, the easiest way to remedy this is to incorporate a stirring device into the liquid bath.

The use of a higher frequency and a spectrum of frequencies would have yielded more accurate results. As was mentioned above, 50 MHz was used since this was the lowest frequency at which there was any discernible absorption. However, for a two millimeter change in transducer-reflector distance (four millimeter path change), the average attenuation for oxygen was 1.0 ± 0.1 dB and for nitrogen, 1.3 ± 0.1 dB. Therefore, these measurements alone were only accurate to within about 10% regardless of the distance errors. As indicated in Eq. (24), the absorption varies as the square of the frequency; consequently, doubling the frequency should theoretically reduce this error to 2.5%. Use of higher frequencies with this apparatus was not possible because the effect of the vibrations was increased enormously and measurements were not feasible. In order to reduce the effects of vibration, spring tensioned quartz rods were made to push down on the reflector; thereby, imposing a positive tension on the wires. It was found, however, that this tension reduced the sensitivity of the paralleling screws, and that the rods merely served as another transmission line for the vibrations to pass through; thus,

aggravating the situation further. Possibly the use of quartz rods in place of the wires would have eliminated much of the vibrational problem; however, parallelism would still have to be adjusted at each reading and the major source of error would still be present.

Finally, it should be mentioned that neither diffraction nor insertion losses contributed significantly to the sound absorption in this experiment. Diffraction losses can be roughly estimated as being one decibel per a^2/λ where a is the transducer radius and λ the wavelength of the soundwave in the sample.[19] For liquid oxygen this loss was approximately 1 dB/800 cm. Since all of the measurements were made on a relative basis utilizing only the first pulse, there would be no apparent insertion loss.

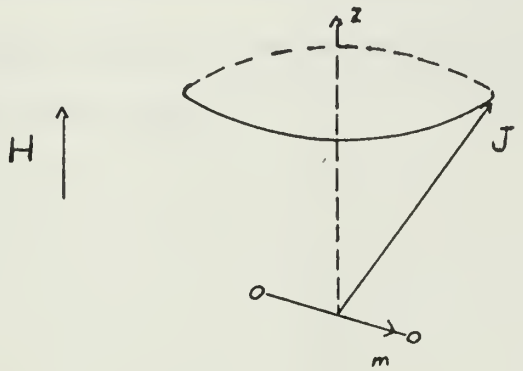
V. DISCUSSION OF RESULTS

The values of absorption coefficients obtained were from 20 to 30% higher than those obtained by Galt; consequently, these two measurements do not agree even to within experimental error. It is difficult to determine which of these measurements is more valid although Galt's values are closer to the theoretical classical values shown in Tables I and II. Since all the values obtained for both oxygen and nitrogen were higher by about 2.5 to 3.0 dB, this would seem to indicate an inherent systematic error in the apparatus which was not accounted for. However, the presence of relaxation effects should not be disregarded since Raman spectra observations have shown the presence of rotational energy levels in liquid oxygen.[20] Another source of excess attenuation could be due to transitions between the diatomic molecular state and some more complex molecular arrangement.

The negative result of the effect of the magnetic field on the sound absorption in liquid oxygen indicates a change in the molecular structure from the gaseous to the liquid state. Henshaw and others[21,22] have already observed this in neutron diffraction experiments, and from their work, the existence of an O_4 molecule is postulated. In order for the observed decrease to place in the gaseous state, the number of degrees of freedom must be restricted in some manner. Van Itterbeek[4] found the effect to be a function of pressure for a given temperature with the effect disappearing at approximately 0.3 atmospheres. He also found that the higher the temperature, the lower the pressure at which the effect disappeared. On the basis of these observations, he concluded that the magnetic field altered the vibrational states since these energy levels are strongly temperature dependent.

Although Van Itterbeek's hypothesis is plausible, it is not immediately

obvious by what mechanism such an alteration would take place. Since the magnetic dipole moment of a diatomic molecule is directed along the interatomic axis and is a result of the electronic states involved in the molecular binding rather than those of the individual atoms, it does not seem likely that the field would produce an interaction, such as a dipole-dipole interaction, between the two atoms which would change the force constant between them. However, it can be seen how the field might affect the rotational states. When a paramagnetic molecule is placed in a constant magnetic field, the total angular momentum vector precesses about the field direction at the Larmor frequency. A schematic of this arrangement is shown below.



Since the interatomic axis is now fixed in space, the rotational degree of freedom which is perpendicular both to the field and to the axis is restricted, i.e., in the direction perpendicular to the plane of the paper in the above figure. This could be the source for the sound absorption decrease which Van Itterbeek observed. The lack of such a decrease in the liquid state is probably due to additional energy levels present in the O_4 molecule.

Further experimentation is needed to determine whether the excess absorption observed in this experiment is because of relaxation effects and to find out which energy states are affected by a magnetic field. Measuring the ultrasonic absorption as a function of frequency would show the existence of relaxation phenomena provided the relaxation frequencies are not too high.

For each temperature and frequency, the magnetic field should be varied over as wide a range as possible. In conjunction with this, an a.c. magnetic field perpendicular to the d.c. field should be employed. This would enable the observation of ultrasonic paramagnetic resonance. It seems reasonable that such an effect might be expected since Zeeman splitting does take place in the gaseous state[23]; therefore, should occur in the liquid state. Extensive electron paramagnetic resonance experiments have been performed on gaseous O_2 [23]; however, very little of this type work has been done in the liquid. A positive result from a combination of ultrasonic and E.P.R. experiments would undoubtedly yield much information about the structure of liquid oxygen which in turn might lead to an explanation of the observed magnetic field effect.

VI. SUMMARY

In general, the equipment fell short of expectations. Even though there is a possibility of relaxation phenomena being present, the accuracy obtained is not compatible with that which should have been acquired with the electronic equipment used. A mechanical apparatus with greater rigidity and one which will maintain parallelism throughout the change in reflector movement is required. The latter stipulation is the most formidable requirement to satisfy in the design of the entire apparatus because of the long distance between the sample and the control mechanisms. Shortening this distance would necessitate a smaller dewar. It is desirable, however, to have as large a volume of cryogenic fluid in the bath as possible since it evaporates so rapidly when being pumped on. A mechanical system designed to eliminate the problems discussed is proposed in Appendix A.

APPENDIX A

The common fault with most apparatus used to measure ultrasonic absorption in cryogenic liquids is the requirement that a parallelism adjustment is needed at each reading.[1,5] It is felt until this problem is circumvented, ultrasonic measurements of this type fall short of the accuracy which is attainable with the pulse-echo technique. A system is proposed here which hopefully would eliminate this drawback and also avoid the other problems which were discussed above.

The description of this system will be made with the aid of Fig. A-1. The sample chamber and the mechanical apparatus are combined into one unit. The sample chamber A is suspended into the cryogenic bath by a large diameter (approximately 1.25-inch I.D.) quartz tube B. The sample chamber is cylindrical in shape with a diameter large enough to allow a small amount of clearance in the thinnest neck of the dewar and a length of six to eight inches. The walls of the chamber are made of 1/8-inch thick brass. The chamber consists of two pieces which can be screwed together and sealed with an O-ring C. In the bottom half of the chamber, the transducer housing D rests in a hemispherical recess. Both the recess and the housing are brass and must be made out of the same piece of material to ensure uniform contraction when cooled.

Inside the transducer housing, a cone shaped electrode is used as described previously. A one-half inch quartz crystal is used instead of a one-inch crystal so that the dimensions of the reflector can be made smaller. The electrode is connected to a co-axial cable, type RG196-U, at the bottom of the sample chamber. The sample chamber itself can be used as ground. Details of this connection are shown in the drawing.

The top half of the sample chamber contains the reflector arrangement. The reflector F is a one-inch diameter quartz rod which is optically flat on the bottom end and cone shaped on the top. This rod fits into a quartz cylinder G which guides the reflector movement. The manufacture of this arrangement is the most critical part of the apparatus. The rod and cylinder have to be ground to fit perfectly so that there is no lateral movement of the rod at all when the piston is being moved longitudinally. The length of the cylinder and piston depends on this requirement. It is estimated that a cylinder about 3" long could be used. The piston would have to extend about one inch beyond the cylinder in its uppermost position and be long enough to be able to travel about 1.5-inch. A friction fit between the two pieces would be desirable and they should both be made from the same piece of quartz to insure uniformity in contraction.

The quartz cylinder G is cone shaped on the bottom to disperse any signals which may hit it. The cylinder is secured to the sample chamber with 6 to 8 redially spaced screws which would fit into threads recessed into the top of the cylinder. Passing through the cylinder are two tubes H and two rods I each 90° apart. (Only one tube and rod is shown in the diagram.) The tubes are used as fill and exhaust lines for the chamber. When not in use, they are to be capped off with 1 - 2 psi overpressure safety valves. This will insure sample purity since air cannot leak in. The tubes are made of stainless steel and sealed at the interface of the sample chamber with an O-ring. The rods pass through the cylinder and are attached to the transducer housing. The top of the rods are attached to small micrometer screws on the cap. With this arrangement paralleling adjustments of the transducer can be made. These rods should be made of quartz and should be just thick enough to be able to sustain the stress put on them (approximately 1/8-inch in diameter).

The top of the piston reflector F is screwed onto a thread protruding from a thinner diameter quartz rod (1/2-inch) K. This rod, in turn, is attached to the bottom of a large micrometer screw which extends down from the cap area. Since the rod K is rigid, movement of the micrometer screw will be accurately transmitted to the reflector piston. Now, instead of parallel movement being required over the whole length of the apparatus, it takes place only in the cylinder G. In order to be able to make absolute distance measurements, two access ports 90° apart, are incorporated into the side of the lower part of the sample chamber (not shown). With this arrangement, the reflector is positioned at a point about 5 mm from the transducer; then, a ball micrometer can be inserted into one of the ports, and an absolute measurement made prior to insertion of the unit into the cryogenic bath. The reflector could be positioned flush with the transducer if the leaf springs holding the transducer were replaced by another type of transducer bond. This would give even a better absolute measurement.

Inside the sample chamber there is a level indicator M. A material whose resistivity is very sensitive in the liquid nitrogen temperature range is mercury doped germanium, and could be used for this purpose. This type of level gauge material is used in the automatic filling of nitrogen dewars in large cryogenic systems. Also, in order to determine the existence of temperature gradients, copper-constantan thermocouples are soldered directly onto the outside surface of the sample chamber at approximately 4 mm intervals. To preclude temperature gradients, two propeller type stirrers are used. The propellers are mounted on shafts which pass through the cap and then to a suitable motor. The shafts should be long enough to position the propellers at the lower end of the wide neck of the dewar.

In addition to all of the attachments and mountings described, the cap must also have a fill line for the dewar, a pipe leading to the pumping line, a BNC connector, and an outlet port for the thermocouple and level gauge wires incorporated. All of these items would come out of the side of the cap in the same manner as in the sample chamber used in this experiment.

It is believed that this system would eliminate the problems encountered in this experiment. The method of measurement is not restricted, and once the reflector and transducer are parellel, this condition should not change with reflector movement provided the piston-cylinder arrangement can be made accurately. Quartz is used extensively because of its extremely low thermal expansion coefficient. Many of the dimensions given are approximate and can only be determined after finding out the details of the piston-cylinder arrangement. All the quartz grinding work would have to be sent out to a commercial company such as the Adolf Meller Company of Providence, R. I. As in any experimental system, this apparatus would have its faults, many of which would not be immediately obvious until the system were actually used. However, it is felt that such discrepancies would be minor and that this unit would yield good ultrasonic attenuation measurements at low temperatures.

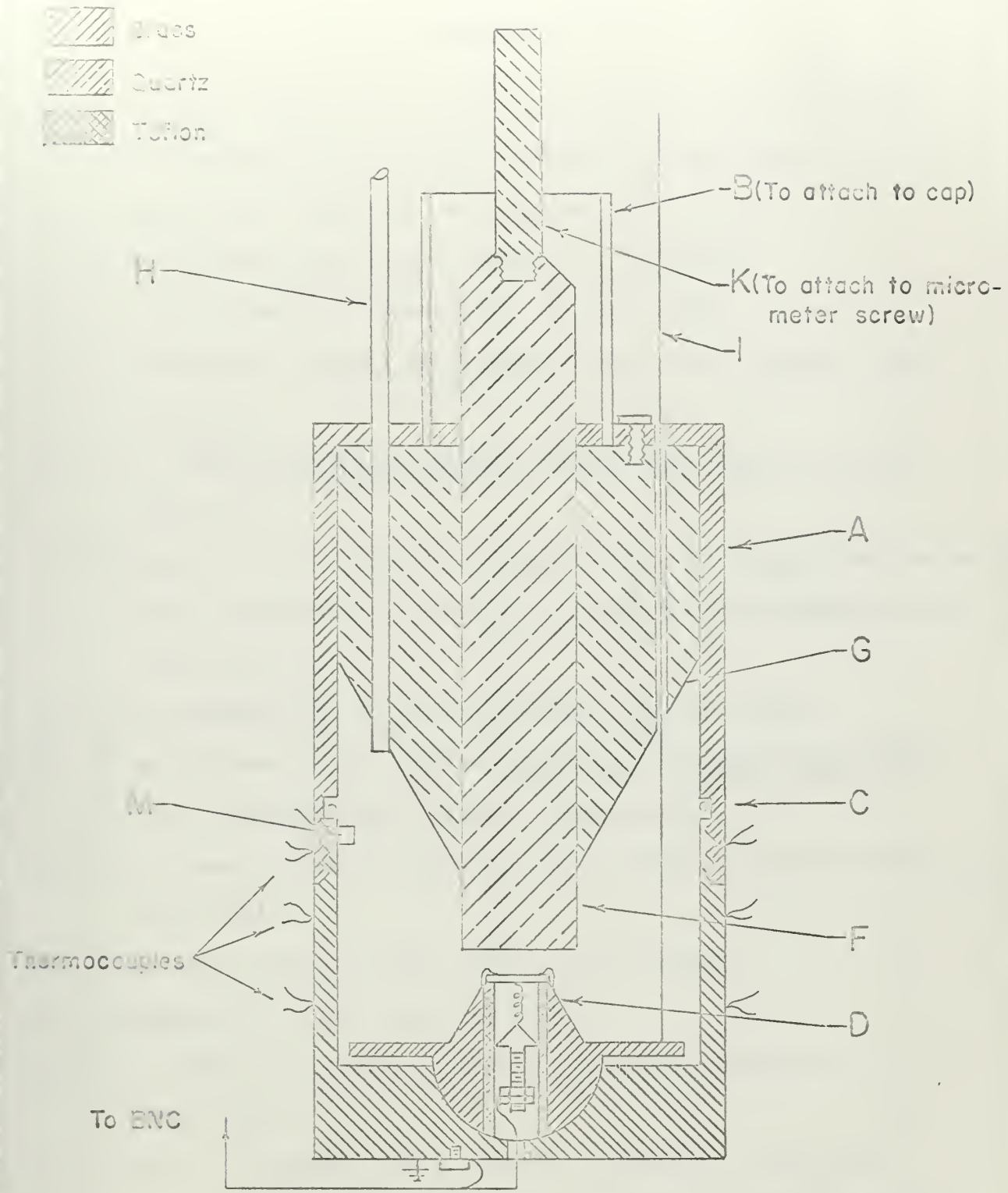


Figure A-1 Sample Chamber

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